

KAOLINITE FORMATION FROM Palygorskite and Sepiolite in Rhizosphere Soils

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Abstract—Palygorskite and sepiolite are fibrous clays that occur mostly in agricultural soils of arid regions. Although many investigations have examined the environmental conditions for the formation and stability of these clays, information on the transformation of these clays in the root zone (or rhizosphere) of agricultural crops is limited. In this study, changes in palygorskite and sepiolite within the rhizosphere of selected agricultural crops were determined and the ability of plants to extract Mg from these minerals compared. Alfalfa, barley, and canola were cultivated in pots under controlled conditions in a growth chamber using growth media that consisted of a mixture of Ottawa sand and clay-sized Florida palygorskite (PFI-1) or Spanish sepiolite (SepSp-1). After 100 days of cultivation, the biomass of plant roots and shoots were determined and Mg uptake measured by inductively coupled plasma analysis of the plant biomass after microwave oven digestion. The clay fraction in each pot was separated from the sand and analyzed using X-ray diffraction (XRD) and examined using transmission electron microscopy (TEM). The XRD reflection at 0.718 nm clearly indicated kaolinite in the rhizosphere after growth of the three crops. Furthermore, hexagonal kaolinite particles were observed, using TEM, and the amount of Mg extracted by the three crops was significantly greater for sepiolite than for palygorskite. Palygorskite and sepiolite kaolinitization in the rhizosphere was apparently due: (1) to high acidity in the rhizosphere caused by root activity and organic matter decomposition; and (2) to fibrous clay destabilization caused by Mg uptake by plants. This study shows that kaolinite in agricultural soils of arid and semi-arid regions might be partly due to neof ormation after fibrous clay dissolution and not entirely inherited from parent materials, as has been suggested in earlier literature.

Key Words—Kaolinite Neof ormation, Palygorskite, Rhizosphere Effects, Sepiolite, X-ray Diffraction.

INTRODUCTION

Palygorskite and sepiolite are Mg-rich fibrous clay minerals which commonly occur in soils and sediments of arid regions. These minerals, particularly palygorskite, occur extensively in the Near and Middle East, North Africa, USA, and Australia (Khademi and Mermut, 1998). Earth scientists, especially pedologists, have studied the origin of and the environmental conditions for the stability of these clays (*e.g.* Bigham *et al.*, 1980; Torres-Ruiz *et al.*, 1994; Akbulut and Kadir, 2003; Daoudi, 2004; Bouza *et al.*, 2007) with almost no attention to the role of plant roots and the associated organisms in rhizosphere soils on their transformation and dissolution.

Fibrous clays are unstable in humid areas (Singer and Norrish, 1974; Bigham *et al.*, 1980; Singer *et al.*, 1995; Neaman and Singer, 2004). Palygorskite and sepiolite are generally believed to weather to other silicate clays, such as smectites, and/or are dissolved out of the soil profile when the mean annual precipitation exceeds

300 mm (Singer and Norrish, 1974; Neaman and Singer, 2004).

Plants alter the weathering conditions, especially within the root zone, primarily by reducing the pH, increasing the numbers of ligands, reducing the concentrations of dissolved elements in the soil solution, and to a lesser extent by changing the redox conditions of the soil environment (Lucas, 2001). Understanding the influence of plants in soil-mineral weathering is generally limited due to the difficulties associated with studying weathering processes in soil-root systems (Kelly *et al.*, 1998).

In order to study the effect of plant roots on mineral weathering, soil scientists have either conducted controlled experiments with pure reference minerals (*e.g.* Spyridakis *et al.*, 1967; Hinsinger *et al.*, 1993; Leyval and Berthelin, 1991; Hinsinger *et al.*, 1992; Hinsinger and Jaillard, 1993) or compared the rhizosphere soil (or soils within 3 mm of the root surface) with non-rhizosphere mineralogy in forest soils (Courchesne and Gorban, 1997; Arocena and Glowa, 2000) and agricultural fields (Kodama *et al.*, 1994; Tributh *et al.*, 1987; Tice *et al.*, 1996). Apparently no such studies have been carried out on palygorskite and sepiolite under controlled conditions or in forest and/or agricultural environments. The objectives of this study were: (1) to determine the transformation of fibrous clays in rhizo-

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Table 1. Elemental analysis (%) of Ottawa sand and fibrous clays used in the experiment.

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	LOI*
Ottawa sand	99.92	0.04	0.01	0.01	0.004	0.004	0.00	0.004	0.05
NH ₄ -saturated palygorskite	58.28	10.20	3.36	1.28	10.31	0.060	0.76	0.560	11.30
NH ₄ -saturated sepiolite	56.02	2.24	0.30	0.06	24.23	0.050	0.06	0.030	16.10

* Loss on ignition at 900°C

sphere soils of selected agricultural crops; and (2) to compare the ability of crops to extract structural Mg from palygorskite and sepiolite.

MATERIALS AND METHODS

Clay minerals and growth medium

Florida palygorskite (PF1-1) and Spanish sepiolite (SepSp-1) obtained from The Clay Minerals Society's Source Clays Repository (at Purdue University) were used in this study. Clay-sized sepiolite particles were separated using sedimentation after grinding the rock chips. In this study, the smectite impurity in the fine clay fraction of the PF1-1 sample was separated using centrifugation and subsequently discarded to collect the coarse clay fraction used in this experiment. Samples of the two fibrous clays were saturated with NH₄⁺ using 1 N NH₄Cl solution. Saturated clays were washed several times with distilled water to remove the excess NH₄Cl. The clay samples were then freeze dried and used in the pot experiment.

Ottawa sand was used as a major plant growth medium. It consists of quartz (SiO₂) and was free of clay minerals and other substances (Table 1). To prepare the Ottawa sand for the pot experiment, it was first soaked in a 0.1 N HCl solution, then washed with distilled water and oven-dried. Both palygorskite and sepiolite were saturated with NH₄⁺ using 1 N NH₄Cl solution prior to total elemental analysis. The elemental composition of reference clays and also that of the Ottawa sand used in the pot experiment were determined following digestion with *aqua regia* and boric acid in a microwave oven (Sawhney and Stilwell, 1994). All the elements were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (PS1000UV, Leeman Labs, Lowell, Massachusetts, USA). The loss-on-ignition values of reference clays and Ottawa sand were measured by the Lim and Jackson (1982) procedure (Table 1).

To prepare peat as organic matter to be used in the pot experiment, it was first passed through a 2 mm sieve. Peat particles of <2 mm in size were then carefully and repeatedly washed with tap water on a 0.05 mm sieve to remove all the clay- and silt-sized particles including any possible minerals associated with the organic tissues in peat. Peat particles with a size ranging from 2 to 0.05 mm were then saturated with NH₄⁺ using 1 N NH₄Cl solution, washed well with distilled water, then

oven-dried and used in the pot experiment. The peat amendment contained too little Mg to contribute significantly to plant Mg uptake (Table 2).

Pot experiment

Pots were filled with a 700 g mixture of clay and Ottawa sand and some were amended with peat, as organic matter, to increase water holding capacity as well as the microbial activity. For peat treatments, the mixture consisted of 18 g of clay, 477 g of 20–30 mesh sand, 198 g of 30–100 mesh sand, and 7 g of 2–0.05 mm-sized NH₄⁺-saturated peat. In treatments without peat, the mixture was 18 g of clay, 482 g of 20–30 mesh sand, and 200 g of 30–100 mesh sand. In each pot, two crop plants were germinated from seeds under growth-chamber conditions. Pots were irrigated with either distilled water as needed or weekly with Mg-free nutrient solution for a period of 100 days. Analytical-grade chemicals were used to prepare the Mg-free nutrient solution according to Stegner (2002) to avoid any impurities such as Mg and Al entering the rhizosphere. We used Stacey barley (*Hordeum vulgare*), Pickseed 2065MF alfalfa (*Medicago sativa*), and Peace canola (*Brassica napus*) to create the three rhizosphere conditions. Three replicates per treatment for a total of 24 pots in a completely randomized design were used in the experiment. At the end of the growing period (100 days), plants were harvested and their shoot and root biomass were measured separately after oven-drying at 75°C for 24 h.

Laboratory analyses

At the end of the experiments, the clay fractions of the growth media in each pot were separated from the Ottawa sand. For the peat-amended treatments, the organic matter was removed from the clay samples using 30% H₂O₂ before mineralogical analyses. In addition, the pH of each pot was measured using a 1:2 mixture of oven-dried rhizosphere soil and 0.01 M CaCl₂ solution. This pH was considered to be the

Table 2. C, N, and Mg contents of the Ca-saturated peat sample used in the experiment.

% C	% N	% Mg
44.8	0.86	0.0084

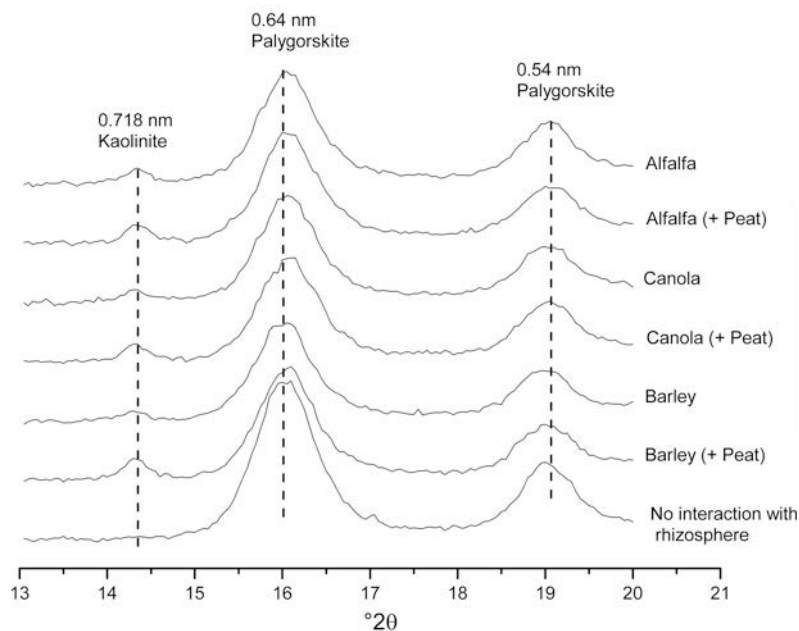


Figure 1. XRD patterns of Ca-saturated palygorskite at ambient temperature and relative humidity before and after 100 days of interaction with different crop rhizospheres with or without peat amendment.

rhizosphere pH at the end of the pot experiment because each pot was entirely filled with plant roots.

The clay-fraction mineral compositions of the rhizosphere soils before and after the pot experiment were determined using XRD. Oriented slides were prepared for both K- and Ca-saturated samples. The Ca-saturated samples were solvated with ethylene glycol (EG) while the K-saturated samples were heated at 550°C. The XRD patterns of the Ca- and K-saturated clay samples were obtained at ambient temperature and relative humidity with a D8 diffractometer, manufactured by Bruker AXS, USA. The $\text{CoK}\alpha$ radiation that was used was generated at 40 kV and 20 mA, collimated to 850 μm , and measured using a General Area Detector Diffraction System (GADDS) 30 cm \times 30 cm detector with a 1024 \times 1024 pixel CCD sensor.

Very dilute clay samples from the rhizosphere soils were dispersed ultrasonically and deposited on Cu grids prior to observation by TEM with a transmission electron microscope (H-7000, Hitachi Co. Ltd., Tokyo, Japan). The Mg contents of plant samples after microwave digestion using concentrated HNO_3 and 30% H_2O_2 were measured using ICP-AES. Reference and blank samples were also run when analyzing the samples with ICP-AES to check the quality of analysis. Each measurement was a mean of three determinations with an acceptable standard deviation.

RESULTS AND DISCUSSIONS

Kaolinite formation in the rhizosphere

Comparison of XRD patterns for the various treatments showed a mineralogical transformation for both

palygorskite and sepiolite. A 0.718 nm XRD peak was observed near the 0.64 nm palygorskite peak in the rhizosphere soil clays of the three crops with or without peat amendment (Figures 1, 2). A prominent 0.718 nm peak was also present near the 0.666 nm sepiolite peak of rhizosphere soil clays from the three crops with peat

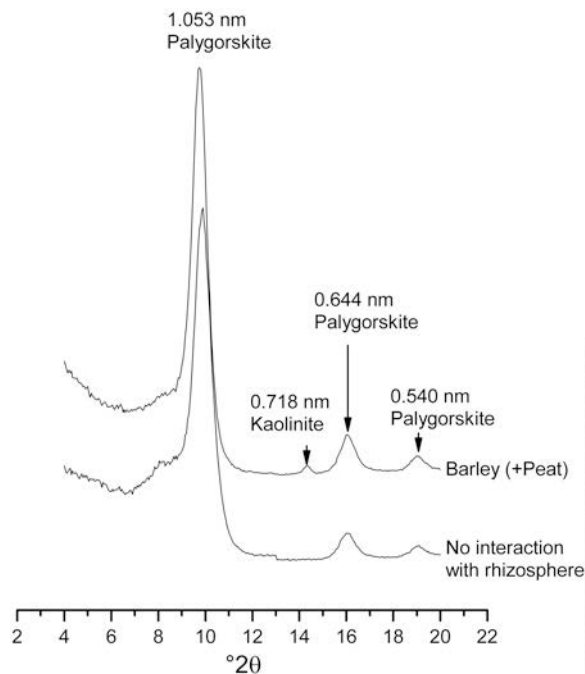


Figure 2. XRD patterns of Ca-saturated palygorskite at ambient temperature and relative humidity before and after 100 days of interaction with barley amended with peat.

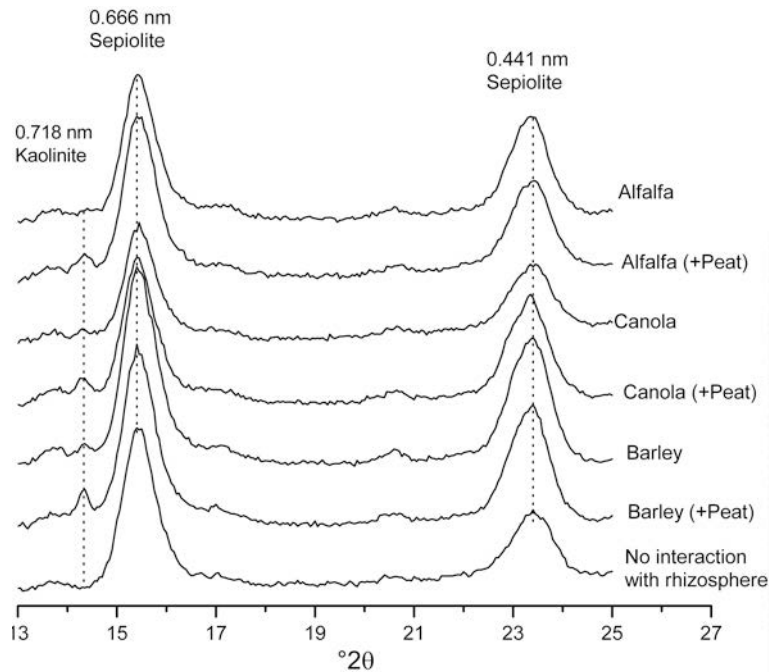


Figure 3. XRD patterns of Ca-saturated sepiolite at ambient temperature and relative humidity before and after 100 days of interaction with different crop rhizospheres with or without peat amendment.

amendment and for the barley and canola crops without peat amendment (Figures 3, 4). This well defined reflection at 0.718 nm was attributed to kaolinite, because the peak remained after solvation with EG but disappeared when K-saturated samples were heated to 550°C for 2 h (data not shown).

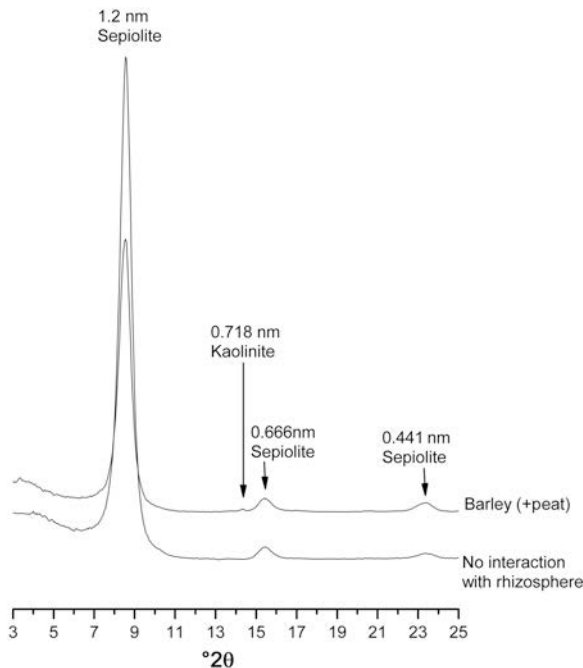


Figure 4. XRD patterns of Ca-saturated sepiolite at ambient temperature and relative humidity before and after 100 days of interaction with barley amended with peat.

The peak intensity (Figures 1 and 2) for the newly formed kaolinite (0.718 nm) was consistently much greater for peat-amended treatment. The clay fraction from the alfalfa rhizosphere soil with no peat amendment showed no reflection in the 0.718 nm region.

The ratio of the kaolinite 0.718 nm peak area to a palygorskite (0.644 nm) or sepiolite (0.441 nm) reference peak was used as an index for the relative quantities of neoformed kaolinite in the rhizospheres of the three crops. Peat amendment led to a greater quantity of neoformed kaolinite in rhizosphere soils of the three crops (Table 3). For both clays, the relative quantity of kaolinite formed after growth of the three crops was not significantly different.

TEM images (Figure 5) of clay-sized particles separated from the rhizosphere depict hexagonal morphology typical of kaolinite (White and Dixon, 2002). These micrographs further corroborate the neoformation of kaolinite in rhizosphere soils of crops containing palygorskite or sepiolite.

Organic compounds in soils are important to weathering of primary soil minerals. Both fulvic and low molecular weight humic acids are considered to be important chemical weathering agents (Ugolini and Sletton, 1991). These acids are water soluble and can contribute significantly to soil acidity by releasing protons into the soil solution. In addition, organic acids act as ligands in the processes of complexation, dissolution, and metal mobility. The extent to which dissolved organic compounds contribute to acidification (by donating protons), chelation (as ligands), or both, appears to be related to the degree of decomposition of the material (Kelly *et al.*, 1998).

Table 3. The ratio of the kaolinite 0.718 nm net peak area to a reference peak in palygorskite (0.644 nm) or sepiolite (0.441 nm).

Crop	Ratio of 0.718 nm peak area to 0.644 nm peak area*100		Ratio of 0.718 nm peak area to 0.441 nm peak area*100	
	Palygorskite + Peat	Palygorskite	Sepiolite + Peat	Sepiolite
Alfalfa	5.55	3.99	5.10	0.00
Barley	5.55	2.63	5.20	1.10
Canola	4.96	3.25	4.50	2.30
Average	5.18	3.29	4.93	1.13

The type of fibrous clay in the rhizosphere, the type of crop, and peat amendment had significant influences on the rhizosphere pH (Table 4). With or without peat amendment, the pH values of the three crop rhizosphere soils with palygorskite were consistently lower than the pH values of rhizosphere soils with sepiolite. This might be due to the low buffering capacity as well as the lesser stability of sepiolite in comparison to palygorskite (Bigham *et al.*, 1980). In addition, potting-soil mixtures with peat amendment had much lower pH values than those without peat amendment. This can be attributed to the production of CO₂ and organic acids as a result of organic matter decomposition by microorganisms (Kelly *et al.*, 1998). Furthermore, the canola rhizosphere had a much lower pH at the end of the pot experiments than those of alfalfa and barley. Several authors have concluded that the ability of different plants to excrete protons and organic acids through the roots is responsible for the low pH values of rhizosphere soils (Spyridakis *et al.*, 1967; Leyval and Berthelin, 1991; Courchesne and Gobran, 1997; Hinsinger and Gilkes, 1997; Kelly *et al.*, 1998; Lucas, 2001; Rufyikiri *et al.*, 2004).

A plot of the relative quantities of neoformed kaolinite vs. the pH values of rhizospheres that contain palygorskite and sepiolite indicates that kaolinite contents increase as the pH decreases (Figure 6a,b). This pH effect can be attributed to the low stability of both palygorskite and sepiolite (Bigham *et al.*, 1980) in comparison to kaolinite at lower pHs (Spyridakis *et al.*, 1967). Both palygorskite and sepiolite become unstable under acidic pH and low Mg and Si activities (Bigham *et al.*, 1980; Golden *et al.*, 1985; Singer *et al.*, 1995; Neaman and Singer, 2004). Singer and Norrish (1974) showed that at silica concentrations normally found in soil solutions, palygorskite would not be stable at pH values <7.7 with high Mg concentrations, or at pH values <9 with low Mg

concentrations. Based on the pH and Mg concentration criteria of Singer and Norrish (1974), the alfalfa, barley, and canola rhizosphere soils in this study provided environmental conditions where palygorskite, and to a greater extent sepiolite, would be prone to dissolution. In previous acid-leaching experiments involving palygorskite, Mg appears to be preferentially released into solution over Fe and Al (Corma *et al.*, 1990). Lower pH in the rhizosphere, especially in peat-amended media, can be due to high CO₂ evolution and exudation of organic acids by roots and microbes as proposed by Lucas (2001). Because the nutrient solution used in this study contained no Mg, the plants must have taken up most of the Mg in the soil solution and accelerated Mg release which caused greater dissolution of palygorskite and sepiolite. The action of organic ligands, such as humic and fulvic acids, as chelating agents would further aid release of structural Mg. These processes explain the greater rate of formation of kaolinite in pots amended with peat compared to pots without peat.

Hinsinger *et al.* (1993) showed that rape (*Brassica napus*) increased the release of K and Mg by a factor of two to four after 4 days when grown in a medium with phlogopite as the sole source of both K and Mg. In a similar experiment using phosphate rock and alumina sand substrate, dissolution of minerals was significantly enhanced by the root growth (Hinsinger and Gilkes, 1997). Moulton and Berner (1998) reported a two- to five-fold increased rate of Ca and Mg release in vegetated vs. barren area on basaltic rocks in Iceland.

Mg uptake by crops

The chemical composition of the plant biomass (weighted average of roots and shoots) at the end of the experiments shows that the three crops grown in sepiolite had significantly greater Mg contents than

Table 4. Mean pH values of the rhizosphere soils of different crops at the end of pot experiment.

Crop	Palygorskite + peat	Palygorskite	Sepiolite + peat	Sepiolite	Average
Alfalfa	6.12	7.95	6.34	7.57	6.50
Barley	6.37	7.66	6.65	8.15	6.77
Canola	4.88	6.69	6.00	8.07	5.44
Average	5.32	7.10	6.25	7.85	

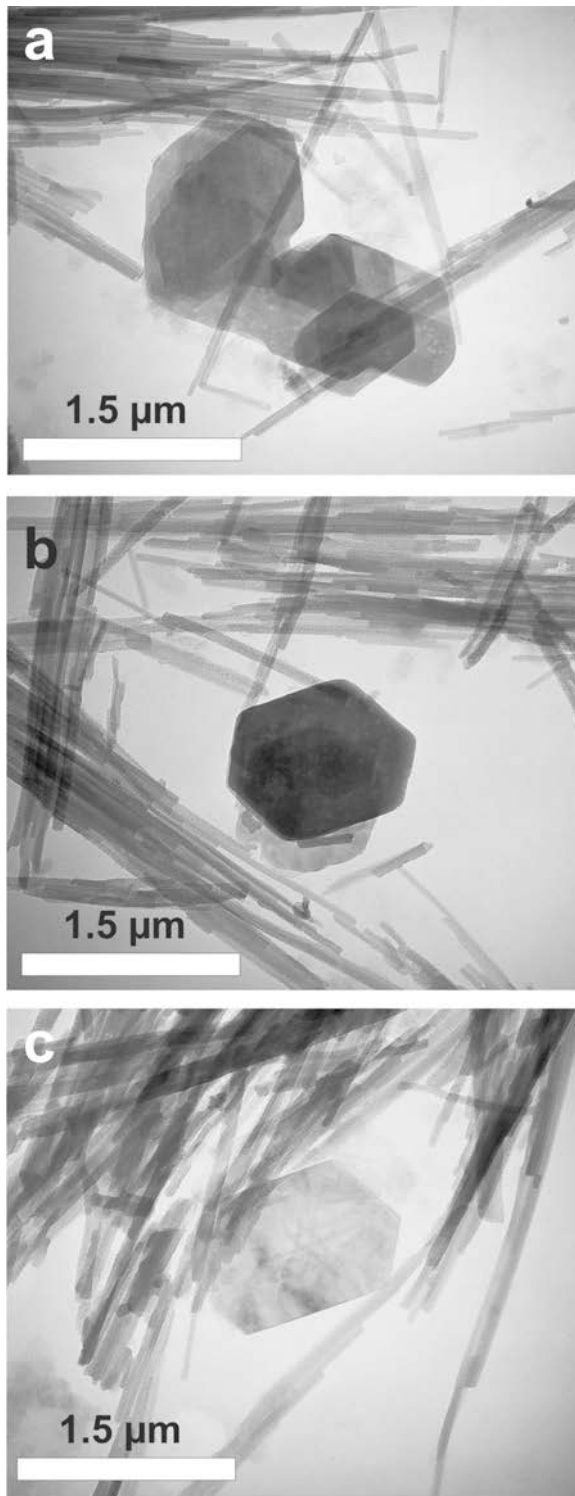


Figure 5. TEM images of clay-sized particles separated from the rhizosphere soils of alfalfa grown on a mixture of quartz sand and palygorskite (a, b) and that of canola rhizosphere containing a mixture of quartz sand and sepiolite (c) showing the neoformation of hexagonally shaped kaolinite as a result of the instability of fibrous clays.

crops grown in palygorskite (Figure 7). Also, peat addition to the growth media resulted in greater Mg concentrations in the biomass than treatments without peat addition. The optimum quantity of Mg for vigorous growth of alfalfa, barley, and most Brassicas (such as canola) are 3–10, 1.5–5, and 4–7.5 mg g⁻¹, respectively (Benton Jones *et al.*, 1991). In comparison to the Mg requirements for optimum growth, alfalfa Mg uptake was not sufficient from either palygorskite or sepiolite, while barley and canola Mg uptake from sepiolite was almost enough to maintain growth, especially when peat was added. The physiological need of plants for Mg continuously decreased the Mg in soil solution released by high acidity and might have accelerated the breakdown of palygorskite and sepiolite and the formation of kaolinite in rhizosphere soils.

Total Mg uptake by the three plants during 100 days of growth followed the same trend with greater Mg uptake by plants grown in sepiolite with added peat (Figure 8). Greater Mg uptake by plants grown in sepiolite than in palygorskite is consistent with earlier findings that sepiolite is relatively unstable in soils even under arid conditions (Khademi and Mermut, 1999),

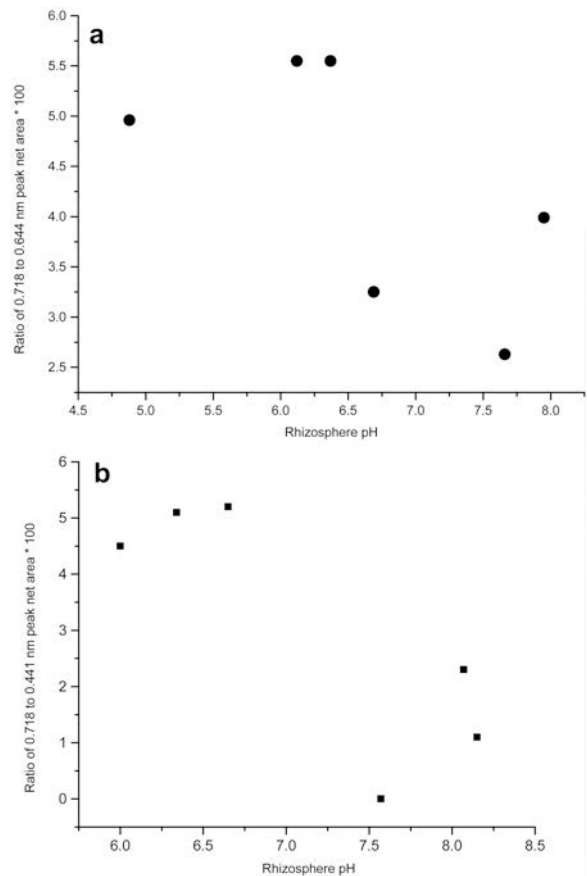


Figure 6. Relationship between the rhizosphere pH and the ratio of 0.718 nm (kaolinite) net peak area to a reference peak in palygorskite (a) or sepiolite (b).

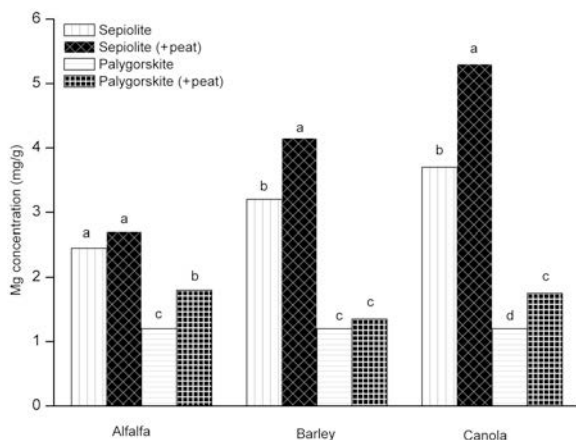


Figure 7. Mean values of Mg concentration in the biomass of different crops grown for a 100 day period in a mixture of quartz sand and either palygorskite or sepiolite with or without peat amendment. In a given crop, the mean values are not significantly different when followed by similar letter a, b, c, or d ($P = 0.05$).

whereas, palygorskite can tolerate environmental zones with up to 300 mm of annual precipitation (Singer *et al.*, 1995; Neaman and Singer, 2004).

CONCLUSIONS

After 100 days of alfalfa, barley, and canola growth, neoformed kaolinite was identified in the root zone of sandy plant growth media that contained palygorskite and sepiolite as the only Mg source. Our study seems to be the first to report the formation of kaolinite from palygorskite and sepiolite in rhizosphere soils supporting agricultural crops. Kaolinization of palygorskite and sepiolite in the rhizosphere appears to be mainly due to:

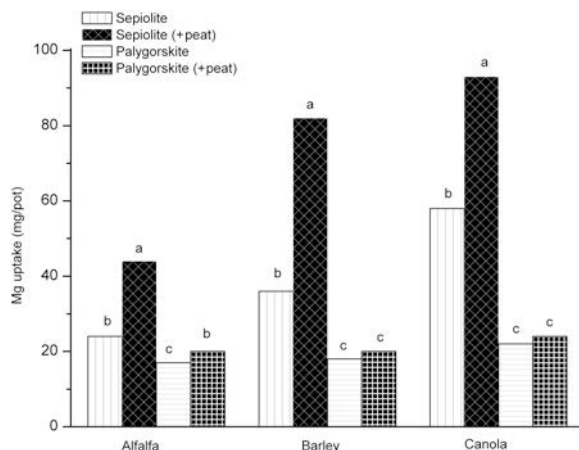


Figure 8. Mean values of Mg uptake by different crops grown for a 100 day period in a mixture of quartz sand and either palygorskite or sepiolite with or without peat amendment. In a given crop, the mean values are not significantly different when followed by similar letter a, b, c, or d ($P = 0.05$).

(1) the acidity of the rhizospheric environment arising from root and microorganism activity and decomposition of organic matter; and (2) of destabilization of fibrous clays as a result of Mg uptake by plants.

Our findings show that the lack of sepiolite and palygorskite in soils of subhumid and humid regions may not be solely due to their chemical instability (Singer and Norrish, 1974; Bigham *et al.*, 1980; Singer *et al.*, 1995; Neaman and Singer, 2004), but also the result of the transformation to other clay minerals such as kaolinite in rhizosphere soils. Furthermore, the occurrence of kaolinite in arid soils does not appear to be entirely due to inheritance from parent materials. Maybe a portion of kaolinite in these soils could be neoformed from the transformation of fibrous clays, a phenomenon not yet suggested by pedologists or soil mineralogists.

Numerous articles have reported palygorskite transformation to smectite under alkaline conditions (Bigham *et al.*, 1980; Golden *et al.*, 1985; Singer *et al.*, 1995), and other investigations have reported the transformation of non-fibrous clays to kaolinite (Lucas, 2001). However, this study appears to be the first to report the neoformation of kaolinite from palygorskite and sepiolite in soil rhizospheres. We believe that kaolinization of fibrous clays in rhizosphere soils is not trivial, especially in arid regions where agriculture has been practiced for hundreds of years. More research is needed to fully understand the mechanism of changes induced by plants and microorganisms, such as organic-acid production and its influence on mineral breakdown. Also, the transformation of both palygorskite and sepiolite to kaolinite seems to play an important role in soils of semi-arid to humid regions with fibrous clay-containing parent materials. Under such conditions, the lack of fibrous clays in soil as well as the formation of kaolinite can be partly attributed to a plant-induced kaolinization process.

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